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A REVIEW OF ALUMINUM OXIDE SENSORS

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Report 88-64-K

ABSTRACT

A literature review was carried out on the performance of aluminum oxide sensors for water vapor pressure (dew point) determinations. Unless adequately aged, significant drifts occur in the sensor output, the drift rate being aggravated by operation at high dew point. For Panametrics sensors, the response time when a dew point decrease occurs is significantly longer than the manufacturer's claim. Recommendations are made for storing the sensor and determining the effect of the sensor filter on the response time.

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EXECUTIVE SUMMARY

A REVIEW OF ALUMINUM OXIDE SENSORS

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Panametrics aluminum oxide sensors are used for the determination of water vapor concentration in several systems in Ontario Hydro's Generating Stations including the Annulus Gas System (AGS) and the Generator Hydrogen System. Reliable operation of these systems require an accurate determination of the dew point of the gas, i.e. water vapor pressure level or humidity.

The tendency for very low readings to be obtained in the field has resulted in questions as to the accuracy and lifetime of the sensors. A program of study on the sensors was initiated by the Chemical Research Department and the results of a literature review are presented in this report. A report on laboratory tests is in preparation.

The aluminum oxide sensor consists of a layer of porous aluminum oxide which is sandwiched between two electrodes. The impedance of the sensor decreases as water vapor pressure increases and is detected with suitable electronic circuitry.

The mechanism of operation involves chemisorption, physisorption, and capillary condensation of water on the oxide and transport of the electrical current by protons (H^+) and hydronium ions (H_3O^+).

Major advantages of the sensor are that cost benefits apply through multipoint monitoring, a sampling system is not necessary, the sensor has a rapid response to increasing humidity and intrinsic safety in the generator hydrogen system is claimed.

Reported response times to increasing humidities fall in the range, less than one minute to about sixty minutes for a $2^\circ C$ accuracy. Early reports of a response time to decreasing dew points of the order of seconds are suspect since a long downwards tail in the response has been confirmed with monitoring for several days at constant dew point. Hence, on exposure to a constant lower dew point, readings are obtained over a range (approx $4^\circ C$) which increases as the time of exposure increases beyond 24 hours. It is recommended that the effect of the protective filter on the response time of the sensor should be quantified.

job	file	date	report no
31-612-050	336.46	July 11, 1988	88-64 -K

Another disadvantage is that the sensor output drifts to lower values with time especially if the sensor is not adequately aged. The drift rate increases as the operating humidity level and temperature increase but reduces with time. As a result of this drift, the error in the dew point indication is larger at high dew point (approx 0°C) than at intermediate values (approx -30°C). A significant effort is required to clean and recalibrate these sensors and test their stability to assure adequate accuracy for a reasonable period after calibration. It is recommended that sensors used in critical applications be stored at ambient humidity for a trial period of about one year prior to use to allow their output to stabilize sufficiently. Following this period they should be stored in a dry environment to maintain their sensitivity and to dry them out for subsequent calibration. Operation at high dew points (above about 15°C d.p.) should be avoided otherwise more frequent recalibration is necessary; if the dew point is high enough for capillary condensation to occur, then accuracy will be relatively lower and response time relatively longer.

For Panametrics sensors no studies were reported to confirm the manufacturer's claim of no effect of carbon dioxide gas on the sensor.

A reading which is low by about 2°C may be expected if these sensors are calibrated at 25°C but operated at about 40°C as in the AGS. A larger drift rate is expected at the higher temperature but the response should be faster.

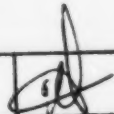
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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 RESPONSE OF ALUMINUM OXIDE SENSORS TO WATER VAPOR	2
2.1 Sensor Signal - Effect of Water Vapor Pressure	2
2.2 Sensor Signal - Drift Down Tendency with Time (Long Term Aging)	2
2.3 Sensor Signal - Short Term Response to Humidity Change	3
2.4 Sensor Signal - Effect of Aging on Response Time	4
2.5 Sensor Signal - Effect of Gas Velocity on Response Time	4
2.6 Sensor Signal - "Hysteresis" with Humidity Cycling	5
2.7 Sensor Signal - Effect of Temperature for Thin Film Sensor	5
2.8 Sensor Signal - Effect of Temperature for Thick Film Sensor	6
2.9 Sensor Signal - Effect of Temperature on Drift Rate	6
2.10 Sensor Signal - Effect of Temperature on Response Time	6
2.11 Sensor Signal - Effect of Chemical Species	7
2.12 Sensor Signal - Effect of Contaminants	7
2.13 Sensor Signal - Effect of Physical Properties of the Sensor	8
2.14 Sensor Signal - Effect of Electronic Circuitry	8
3.0 CONCLUSIONS	9
4.0 REFERENCES	12

APPENDICES

	<u>Page</u>
A. HOW ALUMINUM OXIDE SENSORS ARE MADE	15
A.1 Manufacture - Conventional Method	15
A.2 Manufacture - Electrodes	15
A.3 Manufacture - Semiconductor Method	16
A.4 Manufacture - Post-Anodization Techniques and Stabilization	16
A.5 Manufacture - Electronics	17
B. MECHANISM OF OPERATION OF THE ALUMINUM OXIDE SENSOR	19
B.1 Mechanism - Adsorption Phenomena	19
B.2 Mechanism - Capillary Condensation	20
B.3 Mechanism - Electrical Conductivity Phenomena	21
C. PHYSICAL PROPERTIES OF THE ALUMINUM OXIDE FILM	23
C.1 Physical Properties - Film Thickness	23
C.2 Physical Properties - Pores	23
D. CHEMICAL PROPERTIES OF THE ALUMINUM OXIDE SENSOR	25



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**TO: Dr. D. Mills
Director of Research**

A REVIEW OF ALUMINUM OXIDE SENSORS

V.P. Singh

1.0 INTRODUCTION

Panametrics thin film aluminum oxide sensors are used for the determination of water vapor concentration, dew point or humidity in several systems in Ontario Hydro's Generating Stations. These include the Annulus Gas System, the Generator Hydrogen System, the D₂O Vapor Recovery System and the Instrument Air System.

Questions have been raised as to their accuracy and lifetime in the field. The importance of the accuracy of water vapor concentration determinations in these systems resulted in a program of study on these sensors. The literature review is presented here and a report on laboratory tests carried out on the sensors is in preparation.

The aluminum oxide sensor consists of a layer of porous aluminum oxide which is sandwiched between two electrodes. The impedance of the sensor changes as the water vapour pressure of the surroundings changes and is detected with suitable electronic circuitry. Details of the manufacture including post-manufacture storage to allow stabilization of the sensor output, the mechanism of operation and the physical and chemical properties of the sensor are presented in the appendices.

The mechanism of operation involves chemisorption of water on the aluminum oxide to form metal hydroxides. After completion of the first hydroxyl layer, the first physisorbed layer stacks on it by hydrogen bonding followed by other physisorbed layers. Eventually capillary condensation occurs at relative humidities greater than about 75%. The electrical charge is carried by protons (H⁺) and hydronium ions (H₃O⁺).

The major advantages of the aluminum oxide sensor are that it can be installed in-line without the need for a sampling system, it has a rapid response to increasing humidity and multipoint indications provide cost benefits. A wide dew point operating range, operation at very low dew point (<-76°C) and intrinsic safety with operation in generator hydrogen systems have also been claimed. A major disadvantage is that significant effort is required to clean and recalibrate these sensors and test their stability. Some details on the characteristics of these sensors are given as follows.

2.0 RESPONSE OF ALUMINUM OXIDE SENSORS TO WATER VAPOR

The signal from the sensor for a given water vapor pressure level, the drift of the signal and the response time to a change in water vapor pressure level are dependent on many factors. These are (1) water vapor pressure level including the effects of wide variations, (2) time, both short term response (days) and long term calibration drift (months), including the combined effect of water vapor pressure level and time of exposure, (3) sampled gas velocity (4) temperature (sensor and ambient gas), (5) sensing environment including the signal modifying, corrosive, and fouling effects of gases other than air, carbon dioxide, isotopic species of water, oils, and soluble and insoluble dusts (6) the physical properties of the sensor including porosity and film thickness and (7) the sensor electronics.

2.1 Sensor Signal: Effect of Water Vapor Pressure

Underwood and Houslip (1955) reported that sensor admittance (reciprocal of impedance) increased with increasing relative humidity. The capacitance increased and the resistance decreased as relative humidity increased/Jason(1963), Lai and Hidy(1968), Underwood and Houslip(1955)/. Hence, any decrease in capacitance and increase in resistance for a given humidity level will result in a low reading. Panametrics Inc claim a $\pm 2^{\circ}\text{C}$ accuracy of their sensor above -65°C dew point.

Exposure to high water vapor pressures during the determination of high dew points can produce surface hydroxides and structural changes and crystallization /Rahman and Sing(1979)/. It is possible that the aluminum oxide could dissolve and recrystallize giving a change in surface area and electrical properties. This is usually seen as a continuous drift of the output of the sensor to lower values and the higher the dew point at which the sensor is operated, the more rapid is the drift.

Lin and Senturia (1980) demonstrated that the drift in the resistance of aluminum oxide films was significantly reduced in the absence of an appreciable amount of water. Similarly, a continuous decrease in surface area of the film was observed only if water was present/Harris and Sing (1957)/. However, Chleck and Brousaides(1963) reported that the sensor (2 micrometres thick) can survive direct immersion in water without permanent effect. A similar claim was made by Stover(1963) who reported normal operation as soon as the moisture evaporated.

2.2 Sensor Signal - Drift Down Effect with Time (Long Term Aging)

Aging reduced the water vapor sorption capacity and increased the impedance resulting in low dew point readings/Sze(1970)/. An increase in resistance with time was also observed by Lin and Senturia(1983). Cutting et al(1955) also reported drift to lower readings, ie, that aging reduced the capacitance and increased the resistance obtained at a given dew point. After five months, there appeared to be a shift in the calibration of the sensors to lower readings by about 5°C at 0°C dew point and a 0°C shift at -30°C dew point /Hasegawa et al(1974)/. The larger downward shift at high dew point was also reported by Jason(1963). For Panametrics probes, recalibration interval of six months is recommended for a 2° drift/Verrier and Liut (1988)/.

The output of a newly manufactured sensor can be stabilized by boiling in distilled water for thirty minutes/(Stover(1963a)/. Lin and Senturia(1983) also reported a gradual decrease in the rate at which the impedance increased after about two months exposure to 10°C dew point, ie a tendency towards stabilization. Sensors made with sulphuric acid appear to stabilize after seven months and remain stable

for three months or more while those formed with oxalic and chromic acids showed poor stabilization tendencies/Cutting et al(1955), Jason(1963)/. Only those formed in sulphuric acid remained sensitive at low relative humidities (r.h.). Miyata and Watari(1963) reported that newly manufactured sensors made by anodizing in an oxalic acid layer become stable after storage at room temperature for about four months independent of relative humidity during storage (0 to 75% r.h.). However, no information was given on their sensitivity with time.

According to Bennewitz(1981), pre-aging carried out immediately after manufacture of the sensor has met with limited success due to continuous slow anodization of the aluminum base. This occurs as a result of moisture and residual acid remaining in the aluminum oxide layer after the initial anodization process especially when subjected to an alternating current as utilized in conventional humidity sensor circuitry. However, Lin and Senturia(1980) demonstrated that resistance was still increasing slowly after two months with a film which had all the aluminum converted to the oxide by immersion in hot or boiling water.

Hence, signal drift is also contributed to by other factors in addition to the slow anodization discussed above. Since drift of the sensor impedance with time and hysteresis are found in a variety of sensor designs, they probably result from the characteristics of the moisture sensitive hydrated aluminum oxide film itself rather than the other components of the sensor /Lin and Senturia(1983)/. These may be surface area changes due to crystallization and surface deactivation by hydroxylation.

It is clear that inadequately aged sensors will give a rapidly reducing signal at a given dew point. Steady readings may not be obtained during calibration with such sensors. If readings are taken, the calibrations soon become invalid as the sensor output falls rapidly with time.

2.3 Sensor Signal - Short Term Response to Humidity Change

Harding(1985) reported there is at least one component in the response mechanism exhibiting a long time constant(many days) when a humidity change occurs. This is seen as a changing signal and is often confused with hysteresis. He believed it to be due to the aluminum oxide/hydroxide reaction. The long time response after a step change to a lower dew point has been confirmed at very low dew point by Mehrhoff(1985) and at higher dew point by Singh(1988) who observed a 4° band increasing with time of monitoring beyond 24 hours to greater than 15°C.

Many previous workers monitored the response for less than 24 hours after a step change to lower dew point. This has led to a response time of some seconds for a 63% change with 94% of the response obtained in one minute. These data are suspect because of the long slow drift down of the signal which continues for many days after a step change to lower dew point. Also, the time constant method of summarizing the response data is misleading since the signal does not behave as an exponentially changing one. Furthermore, the response times reported apply to the sensor only and the effect of the sintered metal filter on the response time does not appear to have been quantified.

At low dew point (about -50°C), response time is a minute or more for a 63% change /Chleck(1985), Carr-Brion(1986)/. Mehrhoff(1984) monitored the response for several days at low humidities. Panametrics and Ondyne sensors exhibited a large range of readings (approx 10°C) over the first ten hours as a concentration of 2 microlitres/litre (-72°C d.p.) was approached from a low (0.5 microlitres/litre) or a high (15 microlitres/litre) humidity. He concluded that the main cause of

inaccuracy of the aluminum oxide sensors is a slow response and/or drift especially after exposure to high dew points. A 2°C accuracy required one hour for a -72 to -57°C step change.

At very high dew point, the response was slowed if capillary condensation occurred/Sze(1970)/. Underwood and Houslip(1955) also reported faster response times if relative humidities were kept below 80%. On the other hand, Miyata and Watari(1963) reported that the response time on wet up of the sensors was significantly slowed (>4 min) if the sensors were stored dry.

The possibility exists that condensation will occur on sensors which are transported or stored in winter conditions and then moved into a high humidity plant area. This will result in increased sensor aging and response time unless suitable precautions are taken.

At intermediate dew points, the response time for a 63% change is a few seconds/Chleck(1985), Carr-Brion(1986)/. Stover(1963 b) reported response times of the order of seconds for a two micrometres thick sensor (no filter on probe) for both wet up and dry down even under saturation conditions. Chleck and Brousaides(1963) and Cutting et al(1955) also reported similar response times although the latter workers apparently monitored the dry down response for only ten minutes.

The response time of 1 min for a 63% change to increasing humidity was twice that found for decreasing humidity with a thin film sensor operating at dew points in the range -65 to -90°C/Chleck(1985)/. Lai and Hidy(1968) reported only a 20% difference in the response time to increasing and decreasing humidity provided a sufficient flow rate was maintained past the sensor. The time constant for their device was 0.025 sec (63% change) although the sensor was relatively thick (2 to 4 micrometres). In contrast, Underwood and Houslip(1955) reported that the steady state response time for wet up of a thick film sensor with a graphite outer electrode and no protective filter from a low humidity level to a high humidity level in excess of 80% at 15°C was about 15 minutes. When the change was reversed about one hour was reported for a steady reading.

2.4 Sensor Signal - Effect of Aging on Response Time

Miyata and Watari(1963) reported that for a sensor which had a relatively thicker barrier layer, the response time for a dew point increase was significantly longer after storage in a very dry atmosphere for over 3 months. The response time remained relatively constant over ten months if storage was at about 75% relative humidity. This suggests that if sensors are stored dry to maintain a valid calibration and a high sensitivity, an increase in the response time will be obtained when the sensor is first re-exposed to dew points in the working range.

2.5 Sensor Signal - Effect of Gas Velocity on Response Time

Sze(1970) reported that for a thick film sensor the response time at a velocity of 5m/sec could be about twice that obtained with infinite velocity while the response time at a velocity of 7.5cm/sec would be about 2.5 times that at 15cm/sec. It is believed that the effect of velocity becomes of lesser importance for decreasing dew points due to the slow dry out characteristics of the aluminum oxide itself.

Increased gas rate increases the contamination rate. This results in an increase in the response time and possibly an increase or decrease in the signal depending on the conductivity and surface blocking ability of the contaminant.

2.6 Sensor Signal - "Hysteresis" with Humidity Cycling

The response reported by previous workers as hysteresis may be due to the slow dry down behaviour of the sensor and the different monitoring times used. Results of previous workers are given here as a guide to the variability of the readings obtained at a given dew point.

If the sensor was exposed to high dew points sufficient for capillary condensation to be occurring both large and small differences were reported by several workers between readings taken as dew point was being increased and those taken as dew point was being decreased.

In NBS report 9539(1967), it is reported that if sensors manufactured by Panametrics and believed to be a thin film type were exposed to high humidities especially at near ambient temperature, the difference between the readings at the same dew point but approaching from different directions was about 6°C.

Cutting et al(1955) reported that hysteresis was observable if thick film sensors with graphite outer electrodes were exposed to relative humidities greater than 90% for more than 10 minutes. Sze(1970) tested a Stover type sensor (film thickness <2 micrometres) at relative humidities up to about 85% at which point capillary condensation was claimed to be occurring. He reported a 6°C difference at 12°C dew point between readings taken as dew point was being increased and those taken as dew point was being decreased. Jason(1963) also reported that the sensors were not subject to hysteresis unless maintained in a saturated atmosphere for an appreciable time.

However, results have also been reported for near saturation conditions which are significantly lower than the large hysteresis values given above. Using a Jason type sensor having a outer electrode of silver paint, Sze(1970) observed only a small difference (about 1.5°C) at 50% relative humidity (12°C dew point) although the sensor had been exposed to a relative humidity as high as 85% during the investigation. Short term response tests showed a difference in readings of only about 2°C if the relative humidity approached 88% (about 23°C dew point) /Hasegawa et al(1974)/. At a lower ambient temperature the difference increased as saturation was approached but again the average value was small at 1°C for a -20°C operating temperature.

If the relative humidity was kept below 75% (20°C d. p.), Sze(1970) found that the mass of water sorbed for thick film sensors was reversible. At 0°C dew point, Miyata and Watari(1963) reported a 0.5°C difference in readings. Short term response tests showed the difference in readings was less than 0.5°C if relative humidity was kept below 30% (about 5°C dew point)/Hasegawa et al(1974)/. Hasegawa(1980) reported differences in the 2 to 3°C range for sensors exposed to less than 0°C dew point and as high as 6°C for sensors exposed to higher dew points.

Hasegawa et al(1974) reported that after five months, a sensor which initially showed a 2°C difference in reading when approaching a given dew point from different directions exhibited a 4°C difference at an ambient temperature of 20°C and relative humidity of about 80%.

2.7 Sensor Signal - Effect of Temperature for Thin Film Sensor

For thin film sensors, Chleck(1985) reported a response to absolute humidity rather than relative humidity and that the effect of temperature was not appreciable on the absolute humidity reading.

In an evaluation study by SIREP(van der Laan, 1976), it was reported that a 1°C low reading was obtained at an operating temperature of 40°C increasing to a 3°C low reading at 55°C. These results were obtained with a so called thin film sensor (Panametrics type M22 sensor literature) which has been manufactured since 1966. During the tests it was not clear whether sufficient time was allowed for equilibration, however, additional time would have resulted in an increase in the error.

Harding(1985) also reported that for a thin film sensor (thickness not given) a 10°C temperature increase resulted in a 2°C low reading at about -20°C dew point.

Hasegawa et al(1974) reporting data on five typical commercial sensors showed that a 10°C temperature increase caused a 3°C low reading at 0°C dew point. The error reduced to a one degree low reading at -30°C dew point.

Hasegawa (1980) found that a thin film sensor calibrated at 25°C and reading in a 40°C environment would give a reading (capacitance was measured rather than impedance) of -17°C when exposed to a -10°C dew point.

The data of Lin and Senturia(1983) for a thin film sensor suggest that there is a change in the structure of the hydrated oxide layer with annealing above 40°C. An increase in resistance was observed. Harding(1985) also reported a loss of sensitivity as temperature increased.

2.8 Sensor Signal - Effect of Temperature for Thick Film Sensor

For a thick film (75 micrometres) sensor, Cutting et al(1955) reported that there is little change in the output versus relative humidity over the temperature range 20 to 80°C. A similar dependence was reported by Chleck(1985). However, below 25°C, the output of the probe was reduced for a given relative humidity.

Stover(1963) reported that for a 2 micrometre thick sensor, impedance versus relative humidity was dependent on ambient temperature. In contradiction, Chleck and Brousaides(1963) reported a negligible temperature coefficient with a Stover type sensor.

According to Underwood and Houslip(1955), for a sulphuric acid anodized sensor having an outer electrode of colloidal graphite and what is believed to be a thick film, the overall impedance increased with increasing temperature; capacitance decreased with increasing temperature and the change of capacitance with dew point became insignificant above 35°C; resistance was found to increase with increasing temperature for a given dew point.

2.9 Sensor Signal - Effect of Temperature on Drift Rate

Bennewitz(1981) reported that high temperature causes rapid aging, i.e. reduction of sensor output signal with time, although appreciable amounts of moisture may not be present. Yoshimori et al(1973) showed that residual water was present even at 600°C. Jason(1963) also reported rapid aging at high temperature.

2.10 Sensor Signal - Effect of Temperature on Response Time

Sze(1970) reported that the response time increased as temperature was lowered. Harding(1985) reported that a change in temperature of operation resulted in a long response time(many days).

2.11 Sensor Signal - Effect of Chemical Species

In addition to their possible corrosive nature, chemical species can affect the conductivity of the sensor in a manner similar to that produced by water.

According to Jason(1963), the sensor output is influenced by polar substances especially ammonia which increases the conductivity resulting in high dew point readings. Benzene (almost zero polarization) has a detectable but small effect. Carbon dioxide which is a linear molecule with no appreciable polarization is expected to behave similarly. Panametrics Inc. claim that large concentrations of carbon dioxide have no effect on sensor water vapor indications /Model 700 Operating and Service Manual/. No detailed information was uncovered on the effect of carbon dioxide on the sensor response time or the sensor drift rate.

For CO_2 , Davidson(1973) reported on the existence of a hydrate of CO_2 and H_2O believed to be $\text{CO}_2 \cdot 6\text{H}_2\text{O}$ in the condensed phase. Cherry(1963) reported that molecular association of CO_2 and H_2O occurs in the vapor phase and their data supported the hypothesis that the molecular species is $\text{CO}_2 \cdot \text{H}_2\text{O}$. How this affects the composition of the gas, the species on the oxide surface and the sensor impedance is not known.

2.12 Sensor Signal - Effect of Contaminants

How well the sensor holds its calibration (sensor voltage output vs dew point of exposure) depends on the presence of inert species (eg, dust) in the system and the presence of corrosive chemical species. Hence, it is necessary to test the sensors in the system in which they are to be used to establish calibration intervals.

Dust can block sites from adsorbing water and produce a low signal. Kochsiek(1982) showed the sorption of water is significantly increased on surfaces with oils, dust, etc. Hence, dust can produce a slowing of the response especially if it is hygroscopic (molecular sieve). Similarly, extruding oils, used in the manufacture of sampling system/process tubing can also increase the response time. Intersection of old and new calibration curves indicates possible contamination with moisture adsorbing species. If the dust is conductive (metal particles, carbon) a high reading may be obtained.

Chemical species can attack the materials of construction and increase the resistance. Mercury attacks gold forming an amalgam and destroys the upper electrode contact. It can also form an alloy with the aluminum. Substitution of chromel for gold is possible. In general, the corrosive effect of a contaminant e.g. sulfur species, NO_x , etc., is greatly enhanced by a high humidity level/Harriman(1985). However, ozone (5 microlitre/litre), nitrogen dioxide (200 microlitre/litre) and sulphur dioxide (100 microlitre/litre) had no effect on the element response even at ambient dew points/Chleck and Brousaides(1963). Corrosion usually results in a shift to lower readings over the whole dew point range.

It appears that the sensor should not be cleaned with deionized water only since trace organics can be present. Low conductivity water produced by passing through an organic trap followed by a reverse osmosis and deionization unit is preferred. Care is required in an operational environment to ensure that sealants such as conductive graphite which are used to seal the threaded connection of the sensor to piping are not allowed to contaminate the wiring connector area to the sensor.

2.13 Sensor Signal - Effect of Physical Properties of the Sensor

If the anodization process provides a film thickness less than about 0.3 micrometres, the probe responds mainly to absolute humidity ie, water vapor pressure or dew point. In this case, a low temperature coefficient (ratio of change of dew point indication to change of temperature) is reported when the sensor is subjected to the same dew point but at a different temperature (operating and service manual for model 700, Panametrics, Inc.).

Alternatively, if the anodization process provides a thick film sensor in the range of 1 micrometre or upwards, the sensor shows predominantly relative humidity characteristics, ie, the signal for a given water vapor pressure in a flowing gas decreases as temperature is increased in a very similar manner as the relative humidity decreases/Chleck(1985)/. A low temperature coefficient is usually reported for these thick film sensors when subjected to the same relative humidity but at different temperatures.

Sadaoka et al(1986) showed that high sensitivities are obtained with a thin barrier layer and Stover(1963), Jason(1963) and Sze(1970) reported the same effect with a more porous coating.

A theoretical analysis showed that the response time was inversely proportional to the pore diameter and proportional to the square of the film thickness/Sze(1970)/. However, response time increased in proportion to the increase of adsorbed water. Cutting et al(1955) reported that a thick outer electrode slowed response. A similar claim was made by Stover(1963). Muller(1985) reported that the response time for a dew point change can increase if a protective filter is used. The response time is minimized by a large filter area and a small volume inside the shield. Also, it appears that the total overall porosity of the shield is the important parameter while pore size does not have an appreciable effect.

One manufacturer (Michell) offers a probe with a relatively large sensing area which apparently reduces the effect of contamination allowing longer recalibration intervals.

2.14 Sensor Signal - Effect of Electronic Circuitry

Fleming(1981) reported that the admittance was sensitive to the frequency used to excite the sensor. Sze(1970) working with a 37 micron thick sensor (colloidal carbon outer electrode) found an decrease in impedance as frequency was increased. For a sensor of film thickness which appeared to be about 30 micrometres operating with a porous aluminum outer electrode, Jason and Wood(1955) reported both the capacitance and resistance decreased with increasing frequency. At low relative humidity (<50%), the greatest change was in the resistance with a small change in the capacitance especially for thick probes (about 25 micrometres). Sensitivity appeared to be greatest at about 50 Hz due to significant capacitance change. Underwood and Houslip(1955) also reported that sensitivity decreased as frequency increased. Khanna and Nahar(1984) reported that capacitance and resistance decreased as frequency increased in the range 120 to 1000 Hz.

Drift is increased as a result of continuous slow anodization of the aluminum base layer when subjected to an alternating current as used in conventional circuitry/Bennewitz(1981)/. It can also result from aging of the electronic components in the readout device itself.

Miyata and Watari(1963) working with a sensor having a relatively thick barrier layer indicated that higher sensitivities are obtained if the driving voltage is low provided the relative humidity is greater than 40%. Below 40% relative humidity there did not appear to be a dependence on the voltage used

to excite the sensor. Fleming(1981) also reported that the impedance was sensitive to the amplitude of the applied voltage but details were not reported.

Lai and Hidy(1968) working with a very small sensor (2 to 4 micrometre thick film, graphite upper electrode partially covering the oxide layer) reported that an electric current can heat the sensor. This would improve response time but aggravate drift. Sze(1970) reported that the water vapor concentration is higher in an electric field. Therefore the response time should be faster in adsorption than in desorption since in desorption, water vapor has to overcome an electric field barrier in order to transfer back into the surrounding atmosphere. In addition, the electric field may raise the internal relative humidity to saturation resulting in an increase in response time.

Aging results in a continuously decreasing signal level and a loss of sensitivity especially at low dew points. After some time (years), sensor replacement is required as the electronics become unable to provide suitable signal amplification and processing. For some circuitry also, the probe compensation voltage used is insufficient to suppress the voltage due to the high admittance obtained at low dew point with some sensors.

3.0 CONCLUSIONS

1. The aluminum oxide sensors used in Ontario Hydro Generating stations carry the following manufacturer's claims:

- (a) a thin film design, responsive to absolute humidity rather than relative humidity
- (b) not significantly affected by temperature
- (c) not affected by the carbon dioxide gas used in the annulus gas system.

The extent to which these claims are valid has not been confirmed in the published data. In the case of the effect of temperature, a reading which is low by about 2°C is expected from a sensor calibrated at 25°C but operating at about 40°C as in the Annulus Gas System. Also a larger drift rate but a faster response are expected at the higher temperature.

2. The mechanism of operation involves increasing adsorption of water as dew point increases. Initially chemisorption of water on alumina occurs at low dew point followed by physisorption of water on water as dew point increases. At relative humidities in excess of about 75%, capillary condensation occurs. The charge carriers under the above conditions are believed to be protons(H⁺) and hydronium ions (H₃O⁺).

3. Major advantages include:

- (a) the capability of in-line installation avoiding the cost of a sampling system which can affect accuracy and response time
- (b) multipoint indications which provide cost benefits.
- (c) a relatively rapid response to increasing humidity.
- (d) apparent intrinsic safety in generator hydrogen systems.

4. A major disadvantage is that a significant effort is required to assure accuracy of the indications since the sensor output drifts to lower values with time. The drift rate is larger for newly manufactured sensors and the higher the temperature and the dew point at which the sensor is operated. One study reported that newly made sensors stabilize with time after seven months, ie the drift rate reduces sufficiently for calibrations to be repeatable over several successive months.

The continuous drift of the sensor output to lower values is due to (i) reaction of the aluminum oxide with water which deactivates the surface forming surface hydroxides and (ii) a decrease in surface area on exposure to water vapor and as recrystallization occurs. Continuous slow anodization of the aluminum lower electrode also probably results in a drifting signal.

Recommendation 1 Sensors used in critical applications should be stored for one year at a relative humidity of about 50% prior to use to avoid use of inadequately aged sensors which may have bypassed the manufacturer quality control measures. The validity of this trial storage period should be checked on a few sensors after the first year ie, that sensors do stabilize and that one year storage is adequate for stabilization.

Recommendation 2 All adequately aged sensors should be stored dry to avoid rapid downward drifts in the calibration, to maintain sensitivity, and to ensure adequate dry down prior to calibration.

5. Early reports of a response time of the order of seconds for the time constant (time for 63% of the total change) are suspect since a long tail in the response has been observed and confirmed with monitoring for several days at constant dew point conditions. The indications are that the response is significantly faster if (a) the sensor is exposed to an increase in dew point rather than a decrease and (b) the temperature is increased. The response time appears to be fastest at intermediate dew points. It is slowed at low dew points and at dew points sufficiently high for capillary condensation to occur.

The response times reported for the sensor by previous workers do not include the effect of the protective filter.

Recommendation 3 The effect of the protective filter on the response time should be quantified.

6. At very high dew points, sufficiently high for capillary condensation to occur, a wide range (6°C) of readings may be obtained depending on whether the dew point is increasing or decreasing. At these dew points, the response time is longer and the drift rate more rapid.

Recommendation 4 Operation at high dew points should be avoided otherwise more frequent recalibration will be necessary, accuracy will be low and a slow response will be obtained. Probes which become wet should be dried as soon as possible.

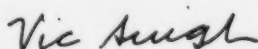
7. Since spring contacts are used in the sensor, transportation should be in a suitably padded container to minimize shock and vibration. Contact problems result in a reduced voltage output over the entire dew point range similar to the effect of corrosion. Care is also required to prevent conductive sealant used at the threads of the sensor body from producing electrical shorts at the cable connector at the head of the sensor.

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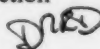


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4.0 REFERENCES

1. J.H.Anderson and G.A.Parks, "The Electrical Conductivity of Silica Gel in the Presence of Adsorbed Water", Journal of Physical Chemistry, Vol 72, pg 3662, (1968).
2. P. F. Bennewitz and M. C. Bennewitz, "Device and Method of Manufacturing a Relative Humidity Sensor and Temperature Sensor", U.S. Patent No 4,288,775 (1981).
3. R. H. Cherry, "Thermal Conductivity Gas Analysis in Hygrometric Applications", Humidity and Moisture, Vol 1, A. Wexler(editor), Reinhold Publishing Corp., New York, pg 372, (1963).
4. D. Chleck and F. J. Brousaides, "A Partial Evaluation of the Performance of an Aluminum Oxide Humidity Element.", Humidity and Moisture, Vol 1, A. Wexler(editor), Reinhold Publishing Corp., New York, pg 405, (1963).
5. D. Chleck, "An Aluminum Oxide Sensor with an Integrated Thin Film Heater", Proceedings of International Symposium on Moisture and Humidity, pg 615, Instrument Society of America (1985).
6. C. L. Cutting, A. C. Jason and J. L. Wood, "A Capacitance-Resistance Hygrometer", Journal of Scientific Instruments, Vol 32, pg 425, (1955).
7. D. W. Davidson, "Clathrate Hydrates", in Water A Comprehensive Treatise, F. Franks (editor), Vol 2, Chapter 3, Plenum Press, New York-London, (1973).
8. I. Emmer, Z. Hajek and P. Repa, "Method of Manufacture of an Electric Humidity Detecting Sensing Element", U.S. Patent 4,441,968, (1984).
9. W. J. Fleming, "A Physical Understanding of Solid State Humidity Sensors", International Congress and Exposition, Society of Automotive Engineers, Inc., (1981).
10. P. Goodman and D.J. Chleck, "Device for Measurement of Absolute Humidity", U.S. Patent 3,523,244 (1970).
11. M.R.Harris and K.S.Sing, "The Surface Properties of Precipitated Alumina", J. Applied Chemistry, Vol 7, pg 397, (1957).
12. J. C. Harding Jr., "Overcoming Limitations Inherent to Aluminum Oxide Humidity Sensors", Proceedings of International Conference on Moisture and Humidity, pg 367, Instrument Society of America (1985).
13. L. G. Harriman III, "Prevention of Metallic Corrosion in Storage Areas", Proceedings of International Conference on Moisture and Humidity, pg 949, (1985).
14. S. Hasegawa, L. Greenspan, J. W. Little and A. Wexler, "A Laboratory Study of some Performance Characteristics of an Aluminum Oxide Humidity Sensor.", N.B.S. Technical Report 824, (1974).
15. S. Hasegawa, "Performance Characteristics of a Thin-Film Aluminum Oxide Humidity Sensor", Proc. 30th Electronics Components Conference, San Fransisco, California, pg 386, (1980).

16. A. C. Jason and J. L. Wood, "Some Electrical Effects of the Adsorption of Water Vapour by Anodized Aluminum", *Proc. Phys. Soc.*, VolB68, pg 1105, (1955).
17. A. C. Jason, "Some Properties and Limitations of the Aluminum Oxide Hygrometer", *Humidity and Moisture*, Vol 1, A. Wexler (editor), Reinhold Publishing Corp., New York, pg372, (1963).
18. Kirk-Othmer, "Encyclopedia of Chemical Technology" 2nd edition, A. Standen - executive editor, Interscience Publishers, New York (1963).
19. V. K. Khanna and R. K. Nahar, "Effect of Moisture on the Dielectric Properties of Porous Alumina Films. Sensors and Actuators, Vol 5, pg187, (1984).
20. M. Kochsiek, "Measurement of Water Adsorption Layers on Metal Surfaces", *Metrologia*, Vol18, pg153, (1982).
21. M.G.Kovac, D.J.Chleck and P.Goodman, "Absolute Humidity Sensors and Methods of Manufacturing Humidity Sensors", U.S.Patent 4,143,177 (1979).
22. M.G.Kovac, D.J.Chleck and P.Goodman, "Absolute Humidity Sensors and Methods of Manufacturing Humidity Sensors", U.S.Patent 4,203,087 (1980).
23. H. M. van der Laan and H. L. Westenberg, "Evaluation of a Hygrometer, Model 2000 with 3 Sensors, model M 22." Report Number E 2275 T 75, SIREP-WIB, (1976).
24. J. R. Lai and G. M. Hidy, "Microsensor for Measuring Humidity", *The Review of Scientific Instruments*, Vol 30, pg 1197, (1968).
25. C. Lin and S. D. Senturia, "The Aging of Hydrated Aluminum Oxide Thin Films", *Sensors and Actuators*, Vol 4, pg 497, (1983).
26. L.Marcussen, "The Influence of Temperature on Effective Diffusivity and Adsorption Kinetics for Humid Air-Porous Alumina," *Chemical Engineering Science*, Vol 29, pg 2061, (1974).
27. T. K. Mehrhoff, "Evaluation of Continuous Moisture Monitors", Report CHM 84- 106, General Electric Co., Neutron Devices Dept.(1984); see also *Rev. Sci. Instrum.* Vol 56, pg 1930, (1985).
28. A. K. Michell, "Capacitive and Resistive Humidity Sensors", *Proceedings of Conference on Humidity Sensors and their Calibration*, National Physical Laboratory, W. H. McGivern (compiler), (1986).
29. A. Miyata and H. Watari, "A Hygrometer which Utilizes an Anodic Oxide Film of Aluminum", *Humidity and Moisture*, Vol 1, A. Wexler(editor), Reinhold Publishing Corp., New York, pg 391,(1963).
30. T.Morimoto, M.Nagao, and F.Tokuda, "The Relation between the Amounts of Chemisorbed and Physisorbed Water on Metal oxides", *Journal of Physical Chemistry*, Vol 73, pg243, (1969).
31. S.H. Muller, "Operational Experience at Sea Locations with a Humidity Sensor Based on the Impedance Measurement of an Electrolyte", *Proceedings of International Symposium on Moisture and Humidity*, pg 643, Instrument Society of America(1985).

32. NBS Report, "Five Aluminum Oxide Humidity Sensors", Report No 9539 (1967).
33. A. A. Rahman and K. S. W. Sing, "Gravimetric Studies of Aging in Microporous Zirconia Gels", *Thermochimica Acta*, Vol 29, pg 277, (1979).
34. Y. Sadaoka, Y. Sakai, and S. Matsumoto, "Electrical Properties of Anodized Aluminum in a Humid Atmosphere," *J. Mat. Sci.*, Vol 21, pg 1269, (1986).
35. T. Seiyama, N. Yamazoe and H. Arai, "Ceramic Humidity Sensors", *Sensors and Actuators*, Vol 4, pg 85, (1983).
36. V.P.Singh, Report in preparation, (1988); see Topical Report on Dew Point Meters, Chemical Research Department Quarterly Progress Report, Mar. (1986).
37. C.M. Stover, "Hygrometer", U.S. Patent No 3,075,385 (1963a).
38. C. M. Stover, "Aluminum Oxide Humidity Element for Radiosonde Weather Measuring Use", *The Review of Scientific Instruments*, Vol 34, pg 632, (1963b).
39. R. A. Strehlow and D. M. Richardson, "Water Chemisorption on Stainless Steel", *Proc. Fourth International Vacuum Congress, Manchester*(1968).
40. M. Sze, "An Anodized Aluminum Humidity Sensor", D.Sc. Thesis, Massachusetts Institute of Technology (1970).
41. C. R. Underwood and R. C. Houslip, "The Behaviour of Humidity-Sensitive Capacitors at Room Temperatures", *J. Scientific Instruments*, Vol 32, pg 432, (1955).
42. T. Verrier and L. Liut, Personal Communication, March 17, 1988.
43. T. Yoshimori, S. Ishiwari, Y. Watanabe, T. Harada, and S. Yamada, "Coulometric Microdetermination of Surface Water on Various Metals and Glasses and of Hydrogen in Beryllium Metal", *Trans Japan Institute of Metals*, Vol 14, pg 396,(1973).

APPENDIX A

HOW ALUMINUM OXIDE SENSORS ARE MADE

A.1 Manufacture - Conventional Method

Two methods have generally been used in the manufacture of these sensors. The older method consists of anodizing (oxidizing at the anode) a high purity, cleaned and degreased aluminum rod or thin sheet in an electrochemical acid cell/Jason(1963), Goodman and Chleck(1970)/. Conditions of cell voltage and temperature and current density are controlled. Sulphuric acid at a certain concentration (15 to 60%) appears to be the preferred electrolyte since it allows sensitivity at low dew points. Stover(1963 a,b) reported that a more suitable oxide coating is made using alternating current.

As discussed below, Sadaoka et al (1986) reported the sensitivity is improved if the barrier layer which is just adjacent to the aluminum metal is removed, for example, by reverse electrolysis in sulphuric acid and chemical etching with 5% sulphamic acid. They also showed that high sensitivities are obtained with low anodization voltages which give a thin barrier layer. High acid concentrations also give a thin barrier layer/Sze(1970)/. A thin barrier layer appears to be preferred also by Michell(1986).

After formation of the film, the anodized aluminum which forms the lower electrode of the sensor is washed and soaked in distilled water for about one or more hours /Jason type sensors(1963), Cutting et al(1955)/. Stover (1963a) reported that boiling in distilled water for 30 minutes seconds stabilized the drift of the output of the sensor with time and this procedure is also performed by others with apparently no change in the oxide thickness/Goodman and Chleck(1970)/. Sze(1970), however, reported that this procedure could cause the closing of pores resulting in reduced sensitivity.

A.2 Manufacture - Electrodes

In early sensors, the upper electrode was formed with silver or colloidal carbon paint/Cutting et al(1955)/. This probably resulted in a long response time, affected the impedance of the sensor and the outer colloidal carbon paint contributed to drift/Sze(1970)/.

Evaporated aluminum has been used as the upper electrode with the advantage that objectionable contact potential is not developed. However, its resistance to natural oxidation is inferior to that of precious metals.

The present technology is to vapor deposit a thin (believed to be about 200 Angstroms thick) conductive, porous, water vapour permeable gold layer onto the aluminum oxide layer. In some cases, a very thin chrome bonding layer is first deposited followed by the gold layer. Stover(1963) reported that too thin a gold coating resulted in a high contact resistance and that too heavy a coating restricted moisture movement. Also, rapid evaporation was necessary to produce a low resistance coating.

Stover(1963a,b) reported that a dip in boiling water for 5 to 60 seconds after electrode deposition resulted in increased sensitivity. Care is required to limit the exposure to boiling water since this often removes the evaporated gold material and the oxide.

A mechanical spring wrapped in gold foil serves as a contact to the upper electrode. A glue may be used but it slows the response at low dew points and may be affected by organics /Chleck(1985)/. The use of spring contacts generally results in the film being thick and of low porosity to prevent shorting of the sensor. Sensors should therefore be transported in suitably padded containers to minimize shock and vibration. Contact problems usually result in low output over the whole dew point range.

A.3 Manufacture - Semiconductor Method

Aluminum oxide sensors are also manufactured by techniques used in the semiconductor industry /Kovac et al(1979),(1980)/. This results in a thin film sensor (about 0.1 to 0.5 micrometres thick) which has a very fast response. Cutting et al (1955) suggested that best sensitivity is obtained with a thin oxide film if low humidities are to be measured. The thin film sensor is more rugged since the upper electrode can be made to overlap a metal pad to which the lead wire can be ultrasonically bonded /Chleck(1985)/. Base materials include silicon with an insulating silicon dioxide or quartz layer/Bennewitz(1981)/. Vapor depositions of aluminum, oxidations (electrochemical or thermal/Lin and Senturia(1983)/), etchings, etc are performed. Aluminum metal which can possibly slowly oxidise with time resulting in a loss of calibration of the sensor can be entirely eliminated /Bennewitz(1981)/. In this case, residual acid remaining after the electrochemical oxidation can be removed with a base solution which also removes any remaining aluminum metal.

A.4 Manufacture - Post-Anodization Techniques and Stabilization

As described above, following anodization, the sensor is washed and may be allowed to sit in water for one hour, and treated in hot water for stabilization or a base solution for some time. The film thickness may be reduced by brushing which also results in a smaller pore mouth diameter/Goodman and Chleck(1970)/. These workers also report that the effect of cracks and fissures in the oxide layer may be reduced by baking the complete sensor including electrodes and leads at 200 to 350°C for 30 to 90 minutes. These cracks trap liquid resulting in a slow response.

It appears the sensors are stored until their output becomes adequately stable. Reasons for instability just after manufacture have not been discussed in the literature but they are probably the same as those producing the slower drift of an aged sensor. These latter include surface area changes, water fixation due to chemical reaction to form hydroxides and slow anodization of the aluminum bottom electrode.

Stabilization requires storage for various times under various conditions of temperature and at ambient humidity. For example, one year at 65°C followed by another period at ambient conditions required for stabilization of the sensor output is believed to be used to get reproducible dew point calibrations (eg <2°C drift over six months). Another manufacturer uses one month at 100°C for what is termed the aging process but it appears that above about 70°C other crystal structures having less active sites and lower surface areas are formed.

Other treatment techniques consist of doping with heavy ions (sodium tungstate/Jason(1963)/) to stabilize the element or lithium chloride to improve the sensitivity of the sensor at very low dew points. Emmer et al(1984) indicated that passivation and tempering improved stability. Passivation of a Stover type probe is carried out by soaking in an aqueous solution of 0.01 to 2 molarity of sodium dihydrogen orthophosphate or silicic acid at 35 to 60°C for 10 to 60 minutes. Tempering is carried out in an inert atmosphere (e.g. vacuum) for several hours at 70 to 100°C.

To prevent mechanical damage, the sensors are often fitted with a sensor shield or a sintered metal filter of about 100 micrometres pore diameter which also slows contamination.

There is a possibility that inadequately stabilized probes could escape quality control measures at the manufacturers plant and be shipped for use. In-station testing for stability would be the most reliable method of assuring quality but would most probably be a labor intensive and periodic procedure over several months. It is recommended that sensors used in critical applications be stored in-station for about one year at ambient conditions prior to use. The validity of this method should be checked on a few sensors after the first year of storage.

A.5 Manufacture - Electronics

The sensor may be excited by an oscillator with a pulse, square or triangular wave input to the electrodes. Various frequencies differing from the line supply of 50 or 60 Hz have been used to reduce signal noise. These include, for example, 77, 111, 770, 4300 (variable pulse width dependent on temperature for temperature compensation) together with an excitation voltage of 1 volt peak to peak.

Underwood and Houslip(1955) showed that a combination of capacitance and resistance gave a better indication of water vapor pressure than either taken singly. The electronics is usually chosen to measure the admittance (reciprocal of impedance) of the sensor when subjected to the above excitation voltage and frequency. The admittance increases as water vapor pressure increases.

Two types of calibration are normally required, ie the sensor voltage output versus dew point calibration followed by the electronics calibration.

For example, the sensor may be calibrated by measuring voltage outputs at a test point (D for the models 600/700, Panametrics) at several known dew points. The data are then empirically fitted to an exponential equation containing three constants (A,B, and C) described by (sensor output voltage - C) = Ae^{BT} where T is dew point ($^{\circ}C$).

The values of A,B and C for the particular sensor are then used in the calibration of the electronics. The value (C) represents a voltage which is electronically subtracted from the output voltage of the sensor. This is done with a probe compensation potentiometer and an electronic calibration switch which substitutes a standard signal from a built in signal generator. A logarithmic amplifier takes the logarithm of the difference which then becomes linear with dew point. The values of A,B, and C are used to calculate zero suppression and range expansion values and the electronics compensation factor which are then used for the adjustment of zero and span potentiometers and the sensor compensation potentiometer. This completes the adjustment of the electronics such that the electronics compensation factor is read out when the calibration check button is depressed. The calibration button is used as time goes by to check that the electronics have not failed and are adjusted for the particular sensor connected to the read out box.

As the sensor ages, its voltage output changes and a sensor recalibration is necessary. A different equation is required to fit the voltage versus dew point data. The electronics must then also be recalibrated.

Newer techniques as reported by Harding(1985) which result in improved accuracy involve the use of microprocessors/erasable programmable read only memories. The calibration information of dew point

versus output can then be stored and the microprocessor can interpolate the data, make temperature corrections and check the stability of the electronic components (electronics calibrations as opposed to sensor output/dew points calibrations). It appears that efforts are underway to correct the reading of the sensor by taking into account its slow response on dry down and also its long term downwards drift provided these can be quantified for the particular sensor/Harding(1985)/. Use of microprocessors allow multipoint indications with accompanying cost benefits.

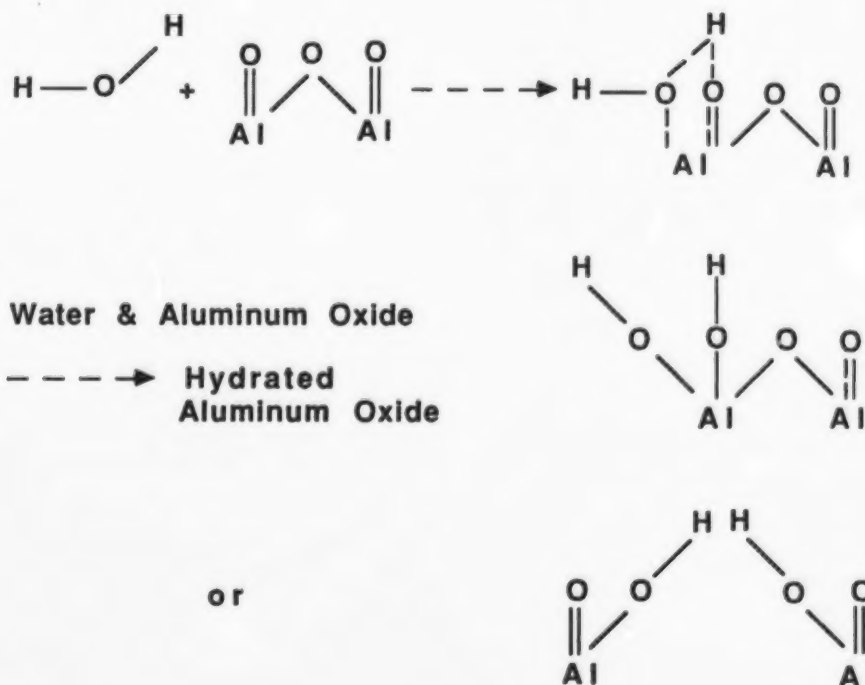
APPENDIX B

MECHANISM OF OPERATION OF THE ALUMINUM OXIDE SENSOR

B.1 Mechanism - Adsorption Phenomena

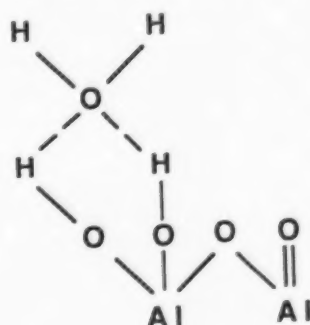
Lin and Senturia(1983) carried out infra-red absorption studies on the hydrated aluminum oxide film. Their interpretation of their results was that the hydrated oxide consisted of fixed water, chemisorbed water and physisorbed water. The fixed light water could not be exchanged on exposure to heavy water (D_2O) vapor and the amount of fixed water remained constant at temperatures up to $200^\circ C$. Yoshimori et al(1973) reported that water was present even at temperatures up to $600^\circ C$.

The chemisorbed H_2O could be removed in the presence of high concentrations of D_2O . However, their results showed that a low concentration of H_2O vapor could not remove chemisorbed D_2O or that the rate was very slow. High concentrations of H_2O ($15^\circ C$ dew point) removed the chemisorbed D_2O in 1.5 hours. Their data suggested that a temperature in excess of $120^\circ C$ was required to reduce the amount of chemisorbed H_2O at an ambient dew point of $10^\circ C$ in 20 minutes. The chemisorption which accompanies dissociation of water molecules forms metal surface hydroxides:



Adsorption measurements with krypton showed the true surface area of the pores was only partially covered with water in the monomolecular adsorption/chemisorption region/Sze(1970)/. It appears that monomolecular adsorption occurs up to dew points of about -10°C . Strelow and Richardson(1968) showed that the amount of water adsorbed at sub-molecular layer quantities on stainless steel increased with time of exposure.

After completion of the first hydroxyl layer, the first physisorbed layer stacks on it with each water molecule being doubly hydrogen bonded to two surface hydroxyls; it appears that the physisorbed water may be only loosely packed covering about 50% of the available surface /Morimoto et al(1969)/.



Water molecules of the next layer are singly hydrogen bonded to the first water layer. The data of Lin and Senturia(1983) suggest that the amount of physisorbed water is continuously reduced above 40°C at 10°C d.p.. Yoshimori et al(1973) found that at room temperature water was present at about 1.5 micrograms/cm² at 50% relative humidity for aluminum oxide films which are believed to be relatively thin. Marcussen(1974) reported that the amount of water vapor adsorbed on alumina was approximately proportional to the square root of the partial pressure of the water vapour and was inversely proportional to an exponential function of temperature.

The chemisorbed and physisorbed layers described above are followed by a few succeeding layers of an ordered ice-like structure and finally liquid-like absorbates.

B.2 Mechanism - Capillary Condensation

Fleming(1981) reported that capillary condensation was not possible in pores of 2 nanometres in diameter at a relative humidity below 40%(dew point = 10°C). The corresponding humidity is probably higher for pores in a typical sensor of about 15 to 50 nanometres in diameter /Sze(1970)/.

Sze suggested also that the relative humidity must be greater than 75% for capillary condensation to occur. The data of Sadaoka et al(1986) suggested that capillary condensation occurred at about 90% relative humidity and above while those of Underwood and Houslip suggested capillary condensation above 80% r.h.. In addition, the electrical field present during measurements of the impedance promotes capillary condensation.

When condensation occurred, the entire pore volume was not filled with liquid water rather the pores appeared to be blocked off with liquid water and only 8% of the volume was filled/Sze(1970)/. Yoshimori et al(1973) found that at room temperature, water was present at about 2.25 micrograms/cm² at 80% relative humidity, cf. 1.5 micrograms/cm² at 50% relative humidity. An extraction temperature of 400°C was used in the determination but it was shown that residual water was present even at 600°C.

Exposure to high water vapor pressures can cause the aluminum oxide to dissolve and recrystallize resulting in structural changes and a change in electrical properties/Rahman and Sing(1979)/. Room temperature aging resulted in a continuous decrease in surface area but only if water was present/Harris and Sing(1957)/. Seiyama et al(1983) suggested that the progressive drift in resistance observed during exposure to high dew points was caused by the gradual formation of hydroxyl groups on the surface. Continuous slow anodization of the aluminum lower electrode is also possible. It is likely this will form new surfaces and increase the sensor signal.

B.3 Mechanism - Electrical Conductivity Phenomena

Explanations have been offered by Seiyama et al(1983) and Fleming(1981). Two types of humidity sensing mechanisms are recognized. These are changes in conductivity due to water chemisorption and increase in ionic conductivity due to water physisorption and capillary condensation in micropores. As relative humidity increases and the amount of water adsorbed increases so does the current flow.

At very low dew points, H⁺ hopping dominates on the metal hydroxide surface /Seiyama et al(1983)/. As the dew point increases and physisorbed water becomes present, both H₃O⁺ diffusion and H⁺ transfer occur on the metal hydroxide surface.

Fleming(1981) reported that the charge carrying species responsible for electrical conduction is the hydronium ion (H₃O⁺); conduction occurs when a proton attaches to a water molecule forming the hydronium ion which then releases another proton to a second water molecule and so on. The current is carried by H⁺ ions when capillary condensation occurs.

It appears that other mechanisms linked to the dissociation of water molecules on the surface of semiconductive oxides resulting in the release of electrons may apply but these are poorly understood.

The explanation is also limited for the increase in capacitance observed as relative humidity increases/Underwood and Houslip(1955)/. Sze(1970) indicated that the dielectric constant which determines capacity depended on the amount of water adsorbed.

Lin and Senturia (1983) reported that the rate of change of resistance decreased substantially if the aluminum oxide samples were stored in dry ambients in between measurements. Harris and Sing (1957) showed a rapid surface area decrease with aging at high humidity. Seiyama et al(1983) suggested that the progressive drift in resistance observed during exposure to high dew points was caused by the gradual formation of hydroxyl groups on the surface. Anderson and Parks(1968) reported that the conductivity of silica gel samples decreased with increasing hydroxyl content. This supports the hypothesis that formation of permanent or more surface hydroxides contributes to the downwards drift which results in a loss of calibration and reduction of sensitivity. Adequately stable sensors which are not in use should therefore be kept dry as recommended by Jason (1963).

Jason (1963) reported an interesting effect in which the sensor itself produces an electromotive force. This was termed the hygroelectric effect analogous to the thermoelectric effect. This effect does not appear to have been exploited.

APPENDIX C

PHYSICAL PROPERTIES OF THE ALUMINUM OXIDE FILM

C.1 Physical Properties - Film Thickness

The sensors are generally termed thin or thick film depending on whether the overall aluminum oxide film thickness is lesser or greater than about 0.3 to 1 micrometre.

The film consists of a thin scalloped barrier layer adjacent to the base metal and an outer porous layer/Sze(1970),Khanna and Nahar(1984)/. The thickness of the barrier layer is 1 nanometre/volt with the barrier layer of a thin film sensor about 1 nanometre thick /Goodman and Chleck(1970)/. It appears that a thinner barrier layer is utilized in modern sensors /Michell(1986)/.

The outer layer consists of approximately hexagonally close-packed fibrous cells containing cylindrical pores normal to the metal surface and extending to the outer surface. Its thickness is 2.5 nanometre/V and is directly proportional to the current density (ma/cm^2) and time of anodization until the maximum value is approached/Sze(1970)/. At this point the rate of dissolution of the oxide equals the rate at which it is formed.

Film thickness and porosity depend on the temperature, composition and concentration of the electrolyte/Jason(1963)/. A decrease in anodization temperature increases the maximum film thickness due to the decreased dissolution rate of the aluminum oxide; an increase in the sulphuric acid concentration also increases the dissolution rate of the oxide layer and increases the thickness of the barrier layer /Sze(1970)/.

The above description of the structure of the oxide layer has resulted in the electrical properties of the film being modelled as a capacitor for the barrier layer in series with a parallel circuit consisting of a resistance and a capacitance for the porous layer.

C.2 Physical Properties - Pores

The porosity of the oxide layer depends on the temperature, composition and concentration of the electrolyte/Jason(1963)/. The porosity of the film is about 40% for anodization at 25°C but the film is usually more porous near the outer surface and porosity increases with the anodization temperature /Sze(1970)/. In one manufacturing process, the temperature of the acid is allowed to rise so that the density of the aluminum oxide layer is less at the lower levels resulting in a more linear response /Bennewitz(1981)/. Stover(1963) reported that a dip in boiling water for 5 to 60 seconds makes the coating more porous and the element more sensitive. It appears that modern sensors are manufactured with a higher density pore structure (more pores per unit area) than the earlier Jason type sensors /Michell(1986)/.

According to Bennewitz(1981), the pores for his particular sensor do not penetrate the entire thickness of the anodized layer (neither do they in the conventional sensor due to the barrier layer), rather a disordered crystalline structure of aluminum oxide is produced. The structure of the oxide layer is normally amorphous/Kirk-Othmer(1963)/. Lin and Senturia(1983) reported there is a change in the structure of the hydrated aluminum oxide above 40°C and an increase in resistance is observed.

There are about 7×10^{10} pores per cm^2 and the distribution of pore diameters on the outer surface is normal/Sze(1970)/. The pores are separated on the average by about 16 nanometres as measured from the centre of the pores /Goodman and Chleck(1970)/.

Khanna and Nahar(1984) reported the pores become trumpet shaped near the outer surface by chemical attack of the acid and it appears that the walls of the pores consist of microcrystallites of alumina and may be pitted. The pores are truncated cones rather than cylinders/Sze(1970)/. The pore diameter is about 50 nanometres (200 times the diameter of the water molecule) at the inlet and reduces to about 15 nanometres at the pore base. No information was uncovered on the effect of the initial grain size of the aluminum used in the anodization process.

APPENDIX D

CHEMICAL PROPERTIES OF THE ALUMINUM OXIDE SENSOR

The composition of the oxide layer is $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($n > 1$). The pores contain acid anions SO_4^{--} , OH^- , and Al^{3+} together with trapped acid. Treatment of the coating in boiling water results in the partial hydration to crystalline mono- or tri-hydrate/Kirk Othmer(1963)/.

The gold and aluminum electrodes are attacked by some materials, for example, mercury which forms an amalgam with both electrode materials. The aluminum electrode is also attacked by sodium chloride and hydroxide and some halogenated compounds especially if significant moisture is present.